THE STUDY OF THE FORMATION OF CHROMATES

BY

H. KAPLON H. M. SCHIFFMAN

ARMOUR INSTITUTE OF TECHNOLOGY 1921

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THE STUDY OF THE FORMATION OF CHROMATES

A THESIS

PRESENTED BY

H. KAPLON AND H. M. SCHIFFMAN

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 31, 1921

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We wish to express our appreciation of the advice and aid of Prof. H. Mc Cormack. We wish also to thank Messrs. Agle, Little, and Vorsheim for their co-operation on the plan and construction of the furnace.

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H. M. Schiffman.

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Introduction.

The purpose of this investigation was to study in detail the production of sodium chromate under various conditions of operation.

This salt is the basic material for the production of all of the numerous chromates and bichromates. Altho it has been manufactured on a large scale for many years, the processes are for the most part crude, laborious, and expensive. Recently a number of patents have been issued on operations which the patentees claim are more efficient than the older methods. The object of this work was to investigate some of these claims in order to substantiate or improve upon the results obtained.

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Present Methods of Production.

The underlying principle in all the methods of preparation is to heat a chrome iron ore, FeO.Cr₂O₃, containing from 40% to 55% Cr₂O₃, with a base or a mixture of bases. Those employed are potassium, sodium, or calcium hydroxide and potassium or sodium carbonate.

The presence of lime makes the mass more porous but less fusible. On the other hand, the addition of sodium chloride or an excess of sodium hydroxide makes the mass more fusible, thus permitting a reduction of the operating temperature.

The ingredients should be finely ground and intimately mixed. Ordinarily the operation is conducted above the fusion temperature of the alkali, and some means of agitating the mixture is required. An air blast is often used, the air being introduced into the molten mass, altho it may be only blown across the surface. Oxygen, as well as air, free from carbon dioxide, has been employed in the same manner

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The chemical reactions are probably as follows:

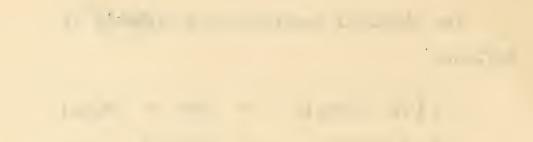
$$4 \left[Fe (CrO_{2})_{2} = FeO + Cr_{2}O_{3} \right]$$

$$2 \left[2 FeO + O_{2} = Fe_{2}O_{3} \right]$$

$$2 \left[2 Cr_{2}O_{3} + 3O_{2} = 4 CrO_{3} \right]$$

$$8 \left[CrO_{3} + 2KOH \right] = K_{2}CrO_{4} + H_{2}O \right]$$

or 4 Fe $(CrO_2)_2$ + 16 KOH + 7 $O_2 = 2$ Fe₂ O_3 + 8 K₂CrO₄ + 8 H₂O.



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The Rotating Furnace.

Before the rotary furnace came into common usage in chemical industries, sodium chromate was made in a reverbatory furnace or in a large iron kettle. Every successful method required some means of agitating the molten mass, usually a blast of air. More recently, however, rotating furnaces have come into common practice. In 1908 a U.S. patent, No. 901,470 was issued on a rotating furnace built for the production of sodium chromate. In Dec. 1913, a U.S. patent, No. 1,081, 625, was issued on a furnace that had an accessory for feeding the raw material. In Mar. 1917, a Swiss patent, No. 73,575, was issued on a furnace that contained an additional feature providing continuous agitation.

With this information available and a general knowledge of furnaces, we decided to obtain a rotary furnace that would on a small scale give the desired results. The attached blue print is the design of the furnace that was to have been used.

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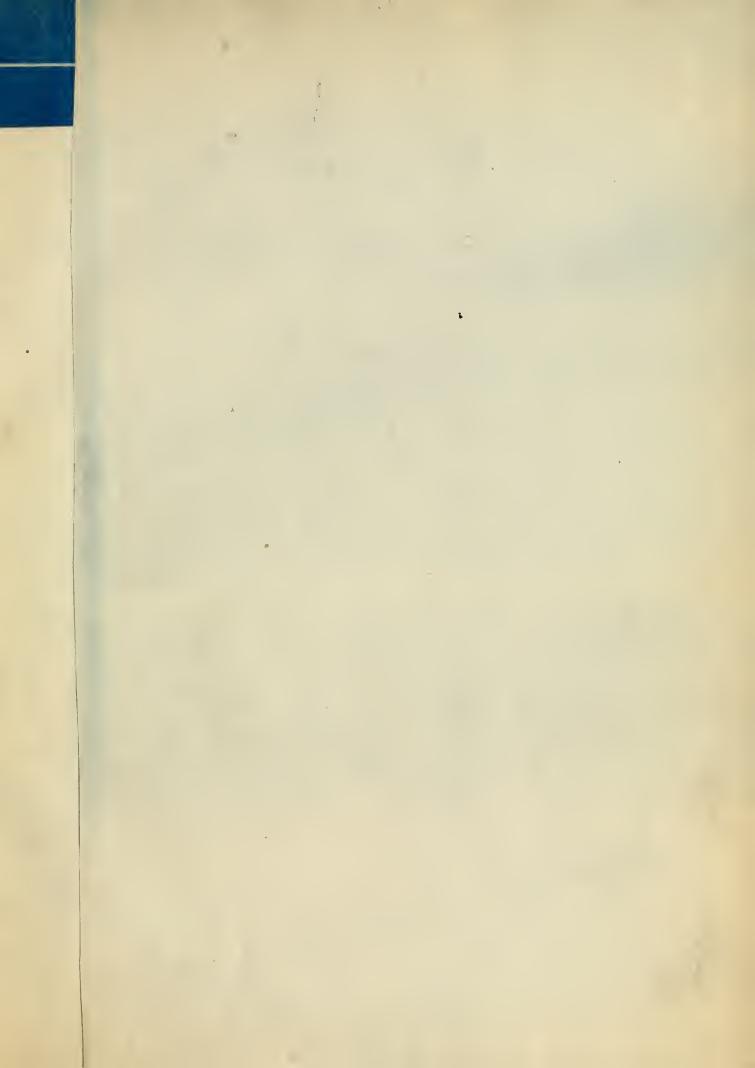
However, we found that this furnace would not be available in time for us to make the desired tests. Consequently, we had to construct one of the materials on hand. Except that the diameter of the furnace used was not large enough, it was satisfactory. If the diameter were greater, a larger charge could have been used, permitting air to be bubbled into the molten mass.

The furnace was driven by a 0.1 H.P. motor at a rate of 9 r.p.m. It was gas fired, city gas being pumped in by attaching a vacuum pump to the city main. The highest temperature attainable was 570°C., which would have been otherwise impossible. A pyrometer and thermo-couple permitted exact control of the temperature. Maintaining the temperature constant was quite easy. In the last test a blast of air was used, a steam pump supplying the air at a pressure high enough to insure rapid circulation within the furnace, altho no effort was made to blow air into the molten mass.

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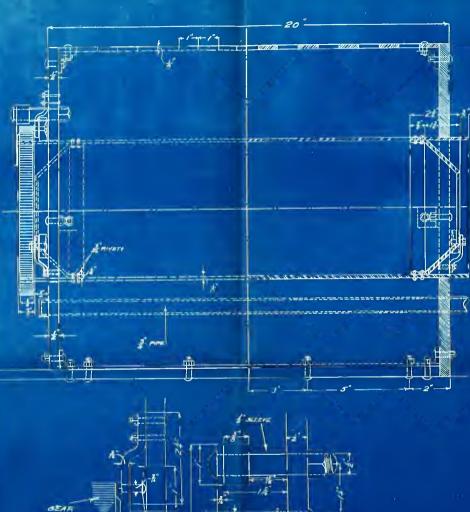
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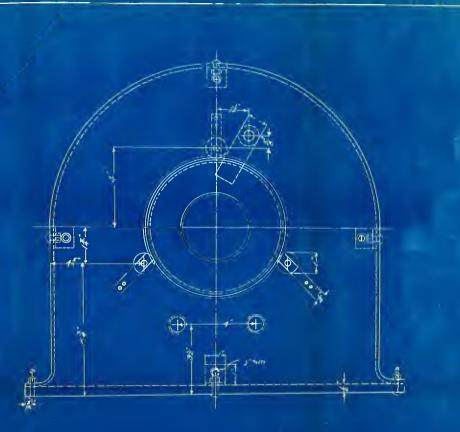
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Our Methods.

We intended to use pure chromic oxide for the first few tests, varying the time, temperature, and quantity of alkali. Later we expected to add iron oxide to determine the effect of it. The final tests were to be made with chrome iron ore.

A close investigation of the quantities of raw materials used in a large number of processes revealed this relation between the concentration of alkali and chromic oxide: if the concentration of the alkali were expressed in terms of chemical equivalents of sodium hydroxide, the ratio of the weight of the caustic soda to that of the chromic oxide averaged very nearly 3 to 1. In a few instances the variations from this were large, but the best practice apparently calls for approximately this value. The theoretical requirements demand a ratio of 1.05 to 1.

Consequently, we decided to use the ratio of 3 to 1 as a basis of calculating our charges. Thus the first run was to have been made with three parts of caustic soda and one of chromic oxide; the

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second was made with 1 pt. of oxide, 1 pt. of caustic soda and 1.32 pts. of soda ash, the equivalent of one part of caustic soda; etc. Owing to the presence of impurities, however, the proportions of the ingredients varied from the basic charge.

The first few tests, of course, formed the basis of the succeeding work.

The temperature used was just sufficient to keep the mass fluid. However, as the concentration of the caustic soda diminishes, the mass becomes more viscous and finally solid. The effect of raising the temperature is described later.

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Methods of Analysis.

The progress of our work was governed by conclusions drawn from chemical analyses. Before each test samples of the raw products and the chrome mix were analyzed. Samples of the batch were removed periodically, at least one every half hour. Each sample was finely ground and bottled, the bottle being labeled and sealed.

A quick method of estimating the percentage of chromate is to dissolve a certain volume of a sample in about 20 c.c. of boiling water. The amount of precipitate remaining is a measure of the incompleteness of the reaction.

For the various analyses a one gram sample was dissolved in water, which was then boiled for half an hour. The solution was made up to 250 c.c. and an aliquot part (25 c.c.) was used for each analysis.

The percentage of chromate formed was determined by titration with N/10 permanganate against the sample, after adding 5 c.c. of standard ferrous sulphate, the former being stand-

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Aardized against a tenth normal solution of sodium oxalate, the result being checked by titration against a weighed amount of chemically pure sodium bichromate. To facilitate the calculations, the strength of the permanganate solution was expressed in terms of percentage of sodium chromate per c.c. of permanganate.

To determine the ratio of soluble chromate to the possible quantity if all the chromium were in that form, an analysis of total chromium was necessary. The most satisfactory method was found to be as follows: **A** one gram sample was dissolved in dilute sulphuric acid and the solution boiled; 10 c.c. of a dilute solution of potassium permanganate were added; the boiling was continued until the purple color disappeared; the solution was filtered and diluted to 250 c.c., an aliquot part (25 c.c.) being analyzed as before.

A knowledge of the nature, as well as the quantity of the alkali, was essential if the proportion for the best yield was to be ascertained.

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We found that the method, by which the percentages of caustic soda and soda ash are determined by titrating against an acid solution and using as indicators phenolphthalien and methyl orange successively, is not reliable for this particular analysis. Consequently, these were separately analyzed.

The caustic soda was determined as follows: to an aliquot part of the water solution, prepared as described above, was added a solution of barium chloride (not more than 10% excess) to precipitate all of the carbonate, a drop of phenolphthalien is added, and enough of a tenth normal solution of oxalic is added until the red color disappears. As the oxalic acid is accurately prepared by dissolving the exact weight of air-dried crystals in water, each c.c. was equivalent to four percent NaOE.

To determine the total alkali, an aliquot part of the water solution is titrated with a tenth normal solution of hydrochloric acid using methyl orange as an indicator. The acid equiva-

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lent of the total alkali minus the acid equivalent of the caustic soda gives the acid equivalent of the soda ash. Of this value, each c.c. corresponds to 5.3% Na₂CO₃.

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Charge No. 1.

The first charge was a mixture of 1 lb. pure chromic oxide and 3 lb. commercial caustic soda which corresponds to the following analysis:

Cr ₂ 0 ₃	25.00%
NaOH	68.00%
Na ₂ CO ₃	3.10%

The furnace had been preheated so that the temperature was 350°C. within a few minutes. Temperatures were recorded every fifteen minutes and samples were taken every half hour. After one and one half hours, the temperature was maintained between 440° and 476° for the next two hours, averaging 450°. During this time the mass was quite fluid, as sodium hydroxide fuses below this temperature.

After about four hours, the material became quite solid and began to cake and form lumps. Evidently as the percentage of free hydroxide diminishes, the fusion point is raised until the entire mass is solid. Thinking that raising the temperature would make the mass fluid, we increased the

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gas supply. During the next hour the temperature rose steadily until 570°C., which was the maximum temperature that could be obtained. During the rest of the run, which lasted seven hours, the temperature was maintained at 565° - 570°.

The analysis of the fourteen samples shows that the percentage of chromate formed varied as follows:

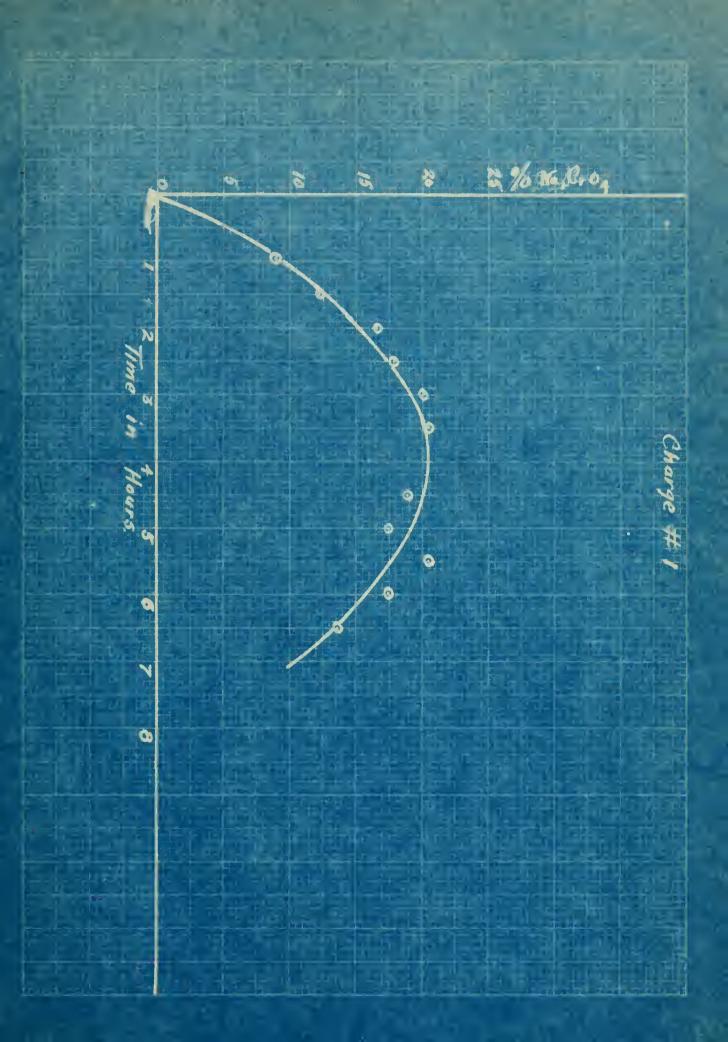
Time	% of Mass	% Converted
1 1/2 hrs.	12.04	
4 ¹¹	20.50	41.40
7 ¹¹	13.60	

The term "% converted" means the percentage ratio of the sodium chromate obtained to that available if the yield were 100%.

The accompanying curve shows the variation, with time, in the percentage of sodium chromate. From this, one can readily see that the percentage of soluble chromate increased to a maximum in four hours, after which it steadily decreased. It was at this time that the temperature was raised, so that the decrease in the percentage of

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soluble chromate may be caused by either, or both, continued heating or the increase in temperature.

As the concentration of chromate increased, the concentration of sodium hydroxide decreased, and vice versa, the minimum alkali being present after 3 1/2 hours.

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Charge No. 2.

This charge was based on the intention to have chemically equivalent quantities of NaOH and Na₂CO₃, the sum being in the proportion of 2.32 of Na₂O (or 3 of NaOH) to 1 of Cr_2O_3 . Its composition was as follows:

Cr ₂ 0 ₃	1 1b.	22.25%
NaOH	1.5 lb.	29.2%
Na_2CO_3	2 lb.	40.8%

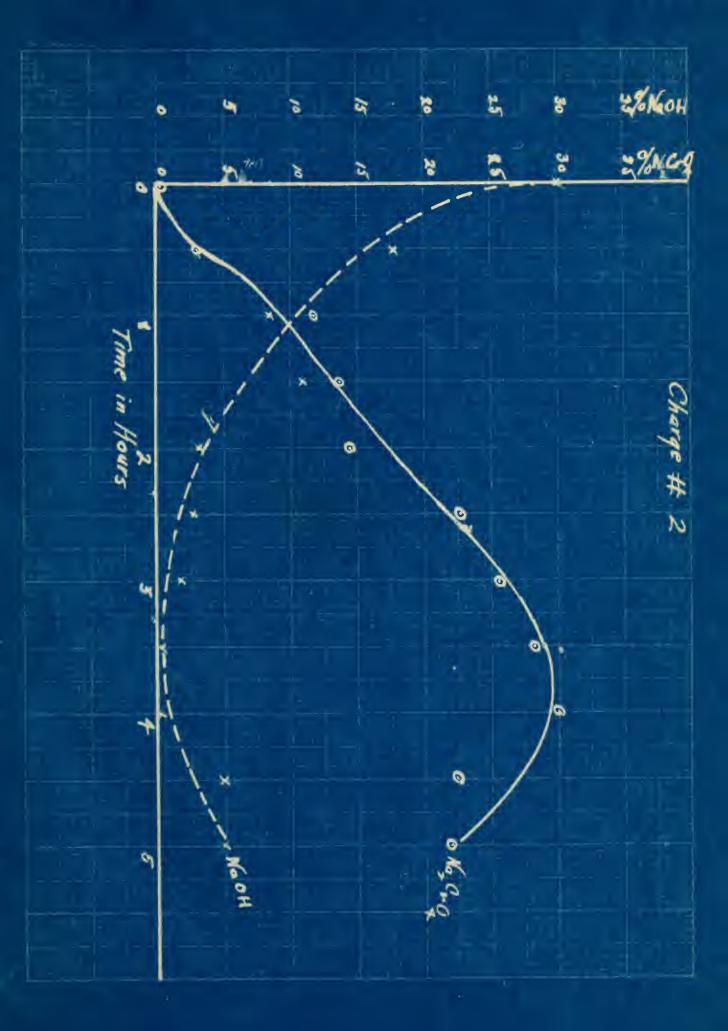
In this run we find a steady increase in the amount of chromate formed until a maximum is reached after four hours; from this point, it steadily decreased. The amount of sodium hydroxide showed a marked decrease, reaching a minimum at the same time the maximum chromate was present. The concentration of the carbonate steadily increased.

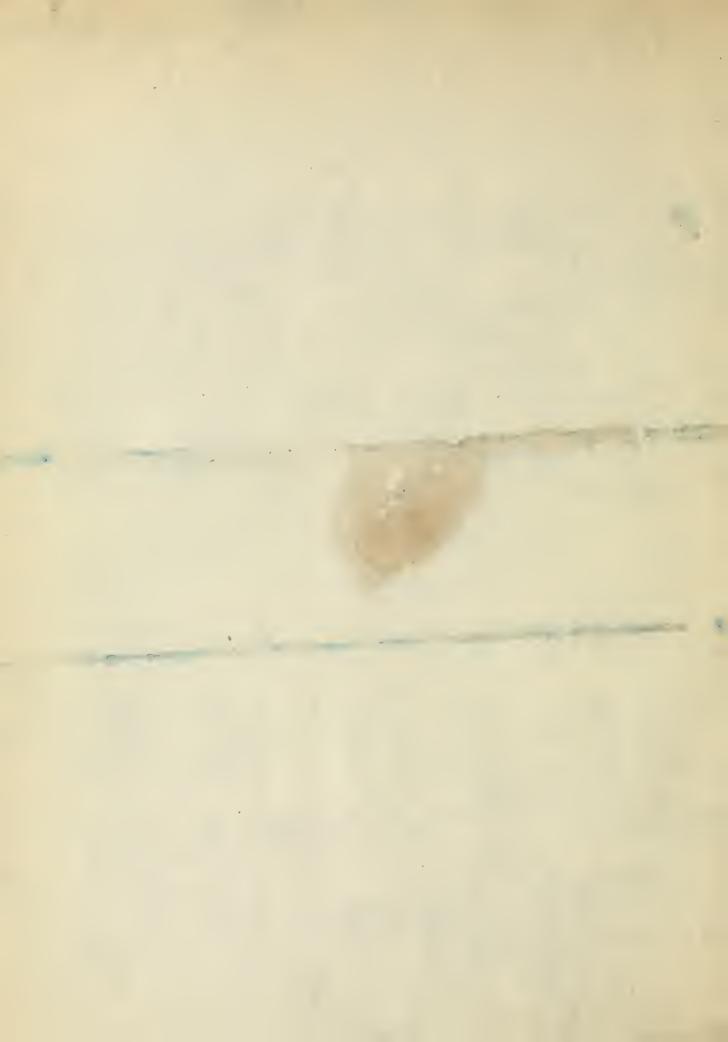
The temperature of the furnace at the start was 330°C., steadily increasing for 1 1/2 hours to a temperature of 470°, then dropping to 435°.

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This temperature was maintained for the rest of the run, which amounted to five hours.

The following values show the variations in the composition:

Time	% of Mass	% Converted
1 1/2 hrs.	13.60	37.50
4 ⁿ	29.60	67.50
5 ¹¹	21.90	49.60

The accompanying curve shows the variation with time in the percentage of sodium chromate. As in the previous run, the concentration of sodium hydroxide decreased, and vice versa, the minimum alkali being present after four hours.

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Charge No. 3.

This charge was based on the intention of having twice as much alkali in the form of soda ash as in the form of caustic soda. Its composition was as follows:

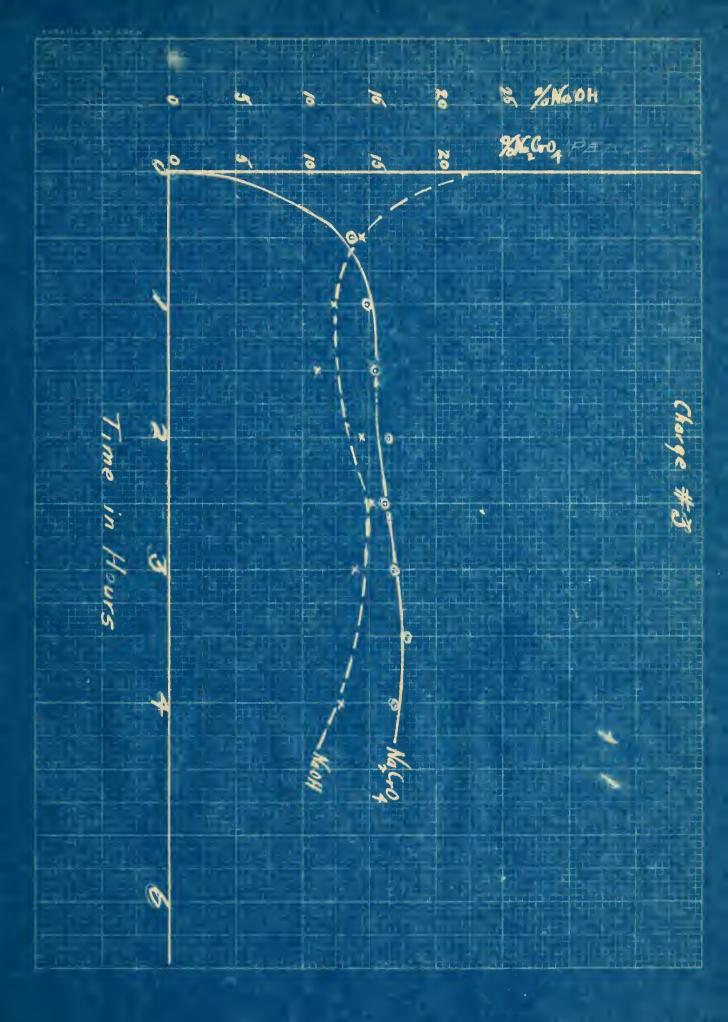
Cr ₂ 0 ₃	1 lb.	21.55%
NaOH	1.12 lb.	19.3 %
Na ₂ CO ₃	2.5 1b.	48.4 %

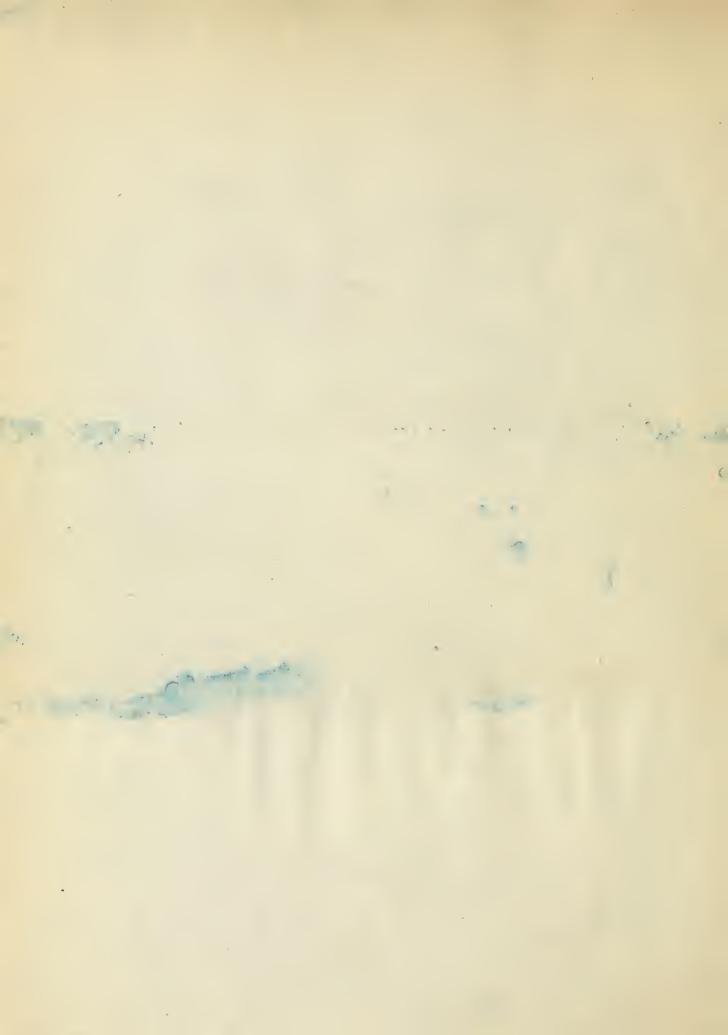
In this run, we find a steady increase in the amount of chromate formed until a maximum is reached after three and one half hours, after which the concentration of chromate decreased. In order to economize, in the time spent on this work, we stopped the run one hour later. As in the previous runs, the amount of sodium hydroxide decreases reaching a minimum at the same time the maximum chromate was present.

The temperature of the furnace at the start was 250°, steadily increasing for one hour, reaching 470°, then remaining about 450°, for the rest of the time. • •

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Time	% of Mass	% Converted
l hr.	13.60	43.00
2 1/2 hr.	16.40	53.00
4 hr.	17.80	57.50

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Charge No. 4.

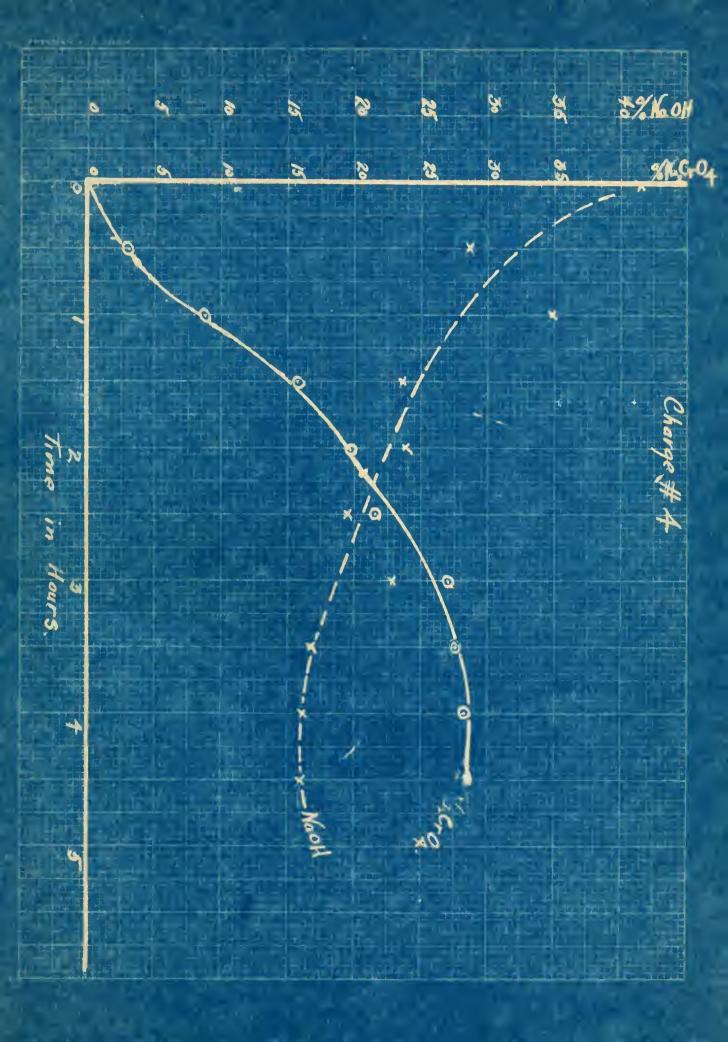
Finding that the amount of sodium chromate decreased with the increase in the amount of sodium carbonate, it was decided to make this run with less of the soda ash. That amount used is the theoretical alkali equivalent, independent of the caustic soda. The analysis was:

Cr ₂ O ₃	1 1b.	22.9%
NaOH	2 lb.	39.9%
Na ₂ CO ₃	1.38 lb.	29.6%

In order that the results would be comparative, it was decided that the temperature should be as near constant as possible for all the runs, This temperature happened to fall between 435° and 475°C.

In this run, the temperature at the start was 275°, rising to a temperature of 465° at the end of the first half hour, and remaining at the average temperature of 455° for the remaining part of the run.

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The amount of sodium chromate formed increased hourly and reached a maximum at the end of the run, which was four hours after we had started. No doubt this run should have been at least one and one half hours longer; however, the results are indicative of what may have happened in a longer run. The analysis of the samples taken gave results similar to the following:

Time	% of Mass	% Converted
1/2 hr.	8.79	27.00
2 hr.	21.60	67.00
3 1/2 hr.	28.20	87.90



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Charge No. 5.

From our work in the first four tests, it became apparent that we were approaching a maximum effect in our yield of sodium chromate due to the composition of the alkali used. Consequently, we decided to use the following percentage of alkali and oxide:

Cr ₂ O ₃	18.79%
NaOH	56.21%
Na_2CO_3	25.00%

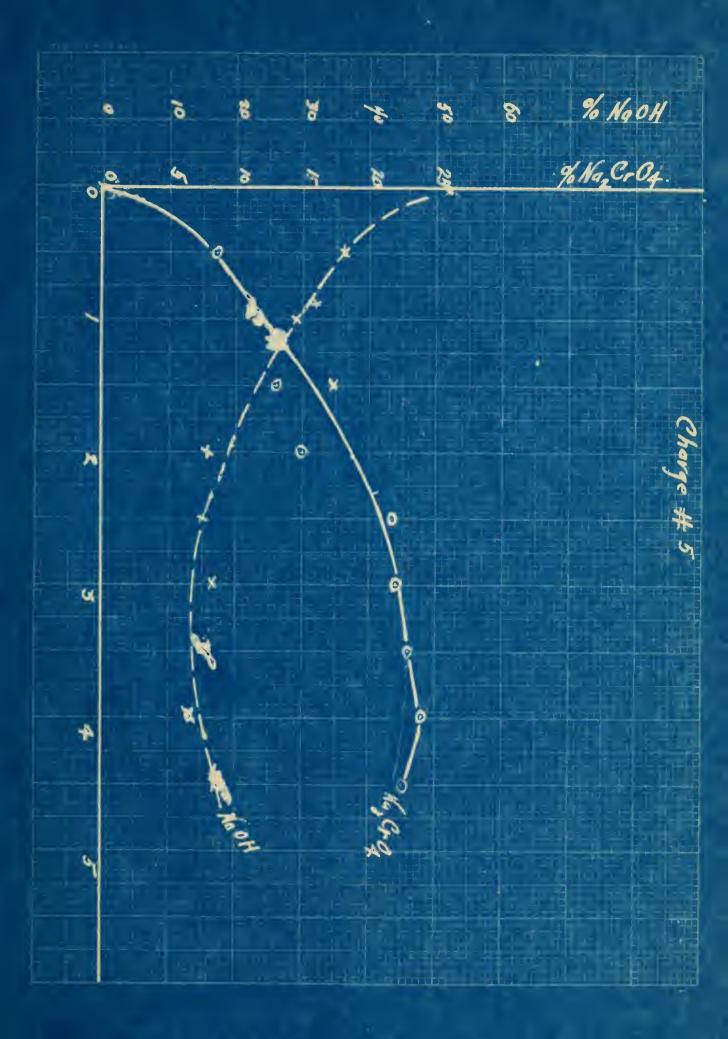
The temperature at the start was 440°C. and was maintained at approximately 10°or 15° higher for the remaining part of the run, which was four and one half hours.

The percentage of chromate formed increased to a maximum at the end of four hours and then gradually decreased. The sodium hydroxide gradually decreased, reaching a minimum when the maximum chromate was present.

The following analyses are submitted as being typical of the results obtained:

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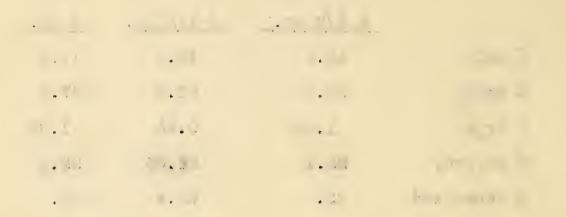


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Results.

	2 1/2 hr.	3 1/2 hr.	<u>5 hr.</u>
% NaOH	16.6	13.2	17.2
% NaCO3	.58.8	61.0	57.2
% Cr ₂ 03	1.85	0.96	1.88
% Na, Cr0.	22.1	24.06	22.6
% Converted	85.	92.4	85.

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Charge No. 6.

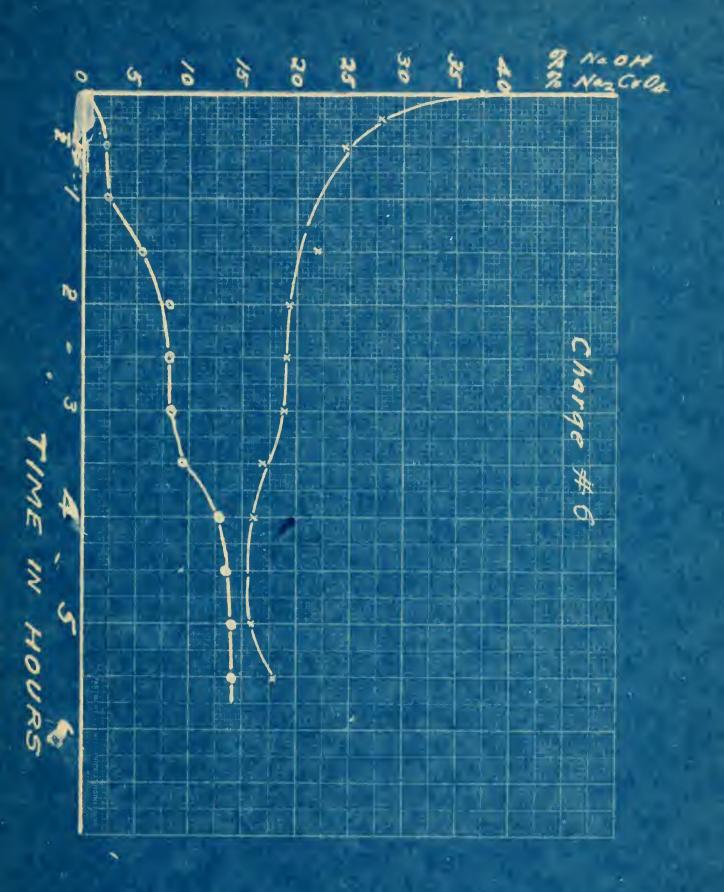
Having established the relation between Cr_1O_3 , NaOH, and Na₂CO₃, which yields the maximum sodium chromate, we decided to make similar tests using chrome ore. Due to the fact that none was immediately available we mixed quantities of ferric oxide and chromium oxide that would be representative of an ore. This should also enable us to determine what influence the ferric oxide had on the formation of the chromates. The composition of the preparation was as follows:

$Cr_2 O_3$	l 1b.	20.30%
Fe ₂ 0 ₃	9/16 lb.	11.40%
NaOH	2 lb.	37.20%
Na ₂ CO ₃	1 3/8 lb.	27.20%

The rate of increase in the percentage of sodium chromate was slower than in the previous tests. As usual a point was soon reached (after: 3 hrs.) beyond which the increase was very slow

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At this point a blast of air was introduced. The air was merely blown across the surface to insure a rapid circulation within the furnace. Had the blast been forced below the surface of the molten mass, probably the oxidation would have been more rapid and more complete.

The following analyses are taken as typical of the results:

	Time	% of Mass	% Converted
]	1/2 hr.	5.5	22.8
2	hr.	8.4	600 400 400 500
* 3	5 11	8.5	
4	L H	12.7	52.6
5	; n	13.8	57.4
Ę	5 1/2 hr.	13.9	57.8

*Air introduced.

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Charge	#1	#2	#3	#4	#5
NaOH	68.5%	29.2%	19.3%	39.9%	50%
Na 2003	3.1%	40.8%	48.4%	29.6%	24.1%
Na Cr O4	25%	22.25%	21.5%	22.9%	18.8%
Max. Yield	43.6%	68.%	57.5%	88%	92.5%

Table of Results.

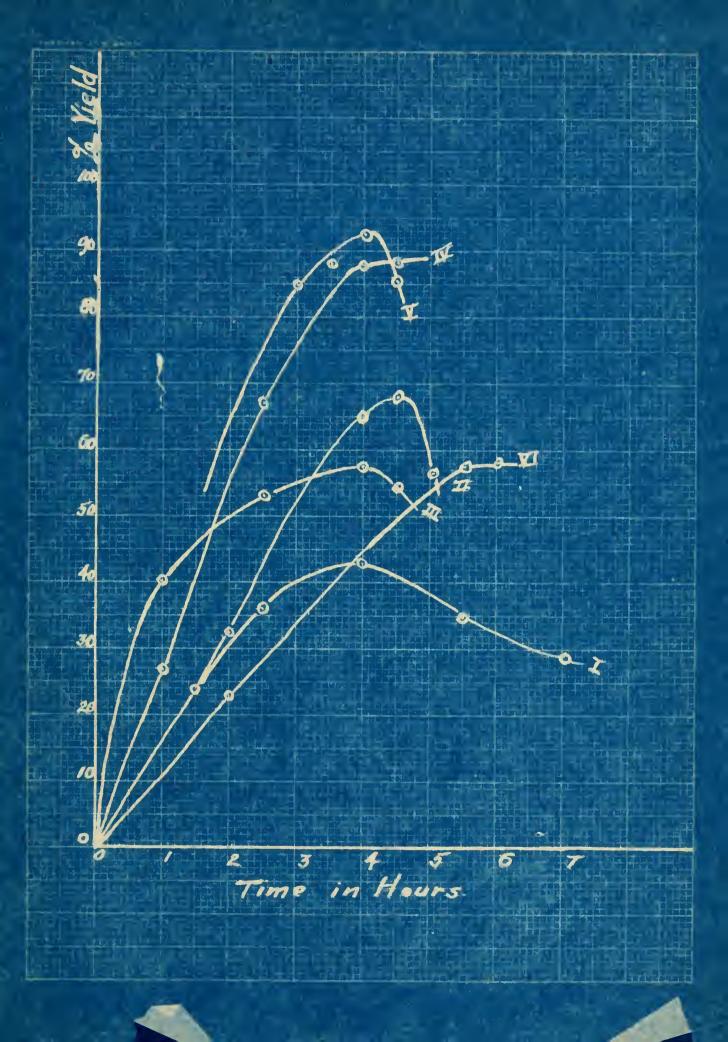
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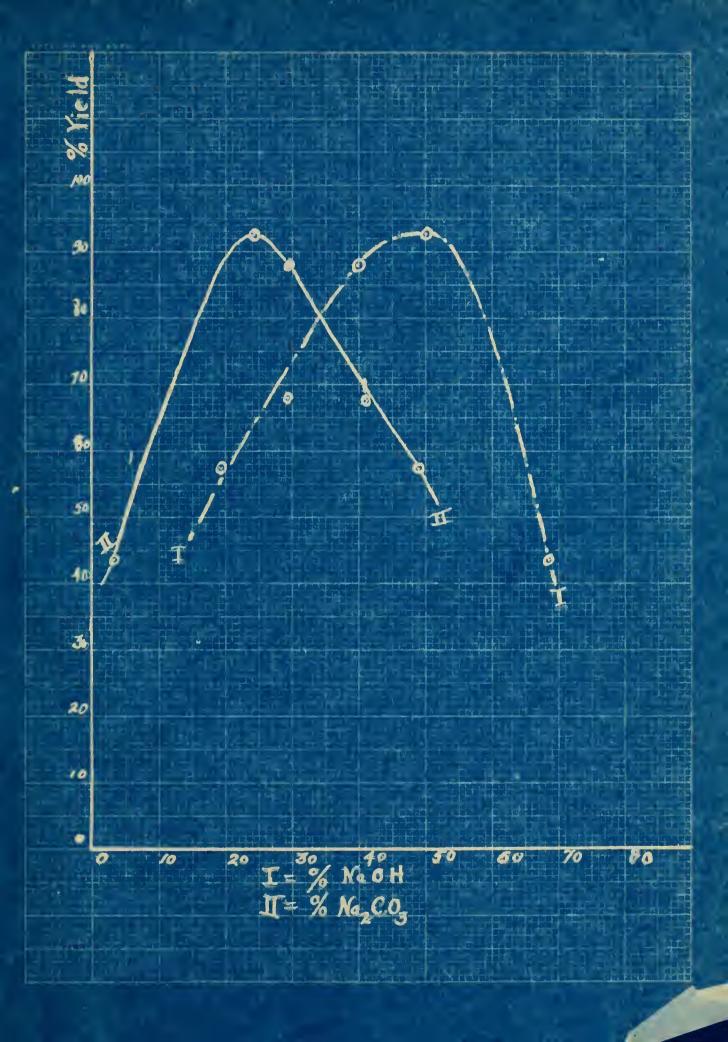
The following curves show the relation between the various tests when the chromic oxide was used. The first shows the yield of sodium chromate, that is the ratio of percentage obtained to the possible percentage, as it varies with the time. The second shows the variation of the yield with the alkalies.

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Conclusion.

The results of our work seem to justify the following statements:

1. To obtain a good yield of sodium chromate a large excess of alkali is required; with certain modifications, the larger the excess, the greater the yield.

2. The use of either caustic soda or soda ash exclusively results in a poor yield.

3. The percentage of soda ash is not appreciable diminished but usually increased.

4. During the first few hours, the percentage of sodium hydroxide decreases rapidly; and if the temperature remains constant, the mass becomes more viscous. Finally the entire mass becomes solid, forming lumps or caking on the wall of the furnace.

5. After this condition is reached, the chromite is but slowly oxidized. After two hours, a maximum conversion to chromate is obtained. Prolonged heating beyond this "peak" or raising the

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temperature tends to reduce the chromate. From the appearance of the charge at this time, we judge that the chromate on the exposed surface is not changed, but that the reduction is caused by the prolonged contact of the chromate with the hot iron at the wall of the furnace.

6. The use of temperatures above 450°C. was found unnecessary; the such temperatures might be beneficial in the early part of the run, after the mass becomes solid they are detrimental.

7. The raw materials should be as rich in the active ingredients as is consistent with economy, because the results indicate that anything that tends to dilute active reagents decreases the rate of reaction.

The economic operation on a commercial scale would require the use of alkali in the ratio of at least three parts of NaOH to one of $Cr_{g}O_{g}$, the alkali being obtained from a mixture of two parts of caustic soda to one of soda ash. As most of the excess alkali is recovered, the use of still

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more caustic soda is reccommended; as the economy of this is questionable, further experimentation would be necessary to determine the expediency of this procedure.

We suggest that several trials be made in which the additional alkali be charged in stages, such as every half hour during the latter part of the run.

As an air blast increases the rate of reaction, as well as the yield, its use would be indispensable. To use air most efficiently, it should be bubbled into the molten mass. This would require a furnace of a larger diameter in proportion to its length; probably one about the shape of a ball mill would be best. Such a furnace would possess less surface in proportion to its capacity, which is a desirable feature. We feel certain operations conducted on the above basis would insure the maximum, as well as the most economical, production of sodium chromate.

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Bibliography.

Nearly all of the information on this subject found in the text books, dealing with the older practice, was unsatisfactory. Consequently, the major part of our investigation of the subject was made in the current literature and the following abstracts:

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Chemical Abstracts(1917) Vol. 11, p. 1733 "Use of NaCl and CaO" Brit. pat. 103,696
Chemical Abstracts(1918) Vol. 13, p. 250 "Mfg. of Alkaline Chromates" B.p. 119,647
Chemical Abstracts(1918) Vol. 13, p. 1374
"Preparation of Alkali Chromates"
Engineering & Mining Journal(1918)
Vol.105 p. 420 . - 1 11

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